

FLUIDIZED BED DESULFURIZATION STUDIES ON ASSAM COAL

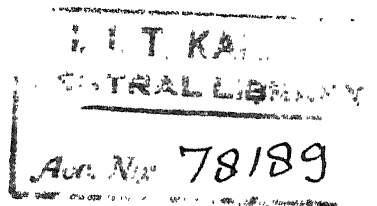
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A B S T R A C T

Desulfurization studies on Assam coals using a fluidized bed reactor were undertaken. Nitrogen, ammonia, and ammonia-nitrogen mixtures at various proportions were used as the fluidizing media. The temperature in the reactor was varied from 400°C to 700°C. The results indicated that

- i) the temperature influences the desulfurization process,
- ii) ammonia is a better desulfurization medium than nitrogen,
- and iii) same desulfurization is effected whether ammonia or ammonia-nitrogen mixtures (in proportions upto about 80 volume percent of nitrogen) were used as the fluidizing media.

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INTRODUCTION

India does not possess any natural sulfur deposits. However, the demand for sulfur is becoming more day by day for its industrial growth. All of its present day sulfur demand is being met by imports. Therefore, the problem of sulfur recovery from various indigenous sulfur bearing raw materials is of particular interest to this country. Coal is one of such material which can offer itself as a potential source for sulfur.

Generally sulfur does not occur in coal as such but exists in the form of compounds. These compounds are present either in organic or inorganic form. Notable inorganic compounds are pyrites and sulfates. Very little is known about the organic form. However, recent studies⁽¹⁾ have shown that organic sulfur is present in the form of thio-ether and bithic-ether.

Apart from economic reasons, the desirability of sulfur removal from coal can be summarized as follows:

1. Coke produced from high sulfur coal will be high in sulfur content. However, for metallurgical purposes coke should be of low sulfur content.
2. Air pollution caused by burning of high sulfur coals is becoming a grave problem.
3. The use of high sulfur coal in boilers for steam generation poses corrosion problems.

Nearly all of the desulfurization work by the previous investigators involved carbonization of coal using fixed bed reactors, with and without certain gases passing through the bed. The method suffers from the disadvantage that, the gas-solid contact is very poor and hence takes a long period of time for sulfur removal from coal. Since a fluidized bed reactor possesses the advantage of good gas-solid contact it was decided to work with such a system. The fluidizing media that were used in this study were nitrogen, ammonia and mixtures of ammonia and nitrogen respectively. Since coals from Assam contain a high percentage of sulfur ranging from 3 to 8%, these coals were chosen for the present investigation. In these coals the sulfur is mainly present in the organic form upto about 90%, the rest being in the inorganic form.

PREVIOUS RELATED WORK

Studies on desulfurization of coal were of industrial importance since a long time. Even today work in this direction is being continued. In this section, some of the studies by the previous investigators are presented.

The earliest work in this field is that of Powell (2,3) in 1923. He studied both the reactions of coal sulfur in the coking process and the desulfurization action of hydrogen on coal. His fixed-bed apparatus consisted of a fused silica tubes of 5/8" in diameter placed inside an electrically heated furnace. The coking charge of 5 gm. of powdered coal was evenly distributed over 4 inches of the middle portion of the tube. From one end of the tube gas was passed and the product gases were collected from the other end.

The reactions of sulfur during carbonization were summarized by him as follows:

1. Complete decomposition of the pyrite and marcasite to ferrous sulfide, pyrrhotite and to hydrogen sulfide occurs. This reaction starts at 300°C and completes at about 600°C. The maximum rate of decomposition is attained in the range of 400 - 500°C.
2. Sulfate sulfur is reduced to sulfides. This reaction completes at about 500°C.
3. Major portion of the organic sulfur decomposes to hydrogen sulfide. This decomposition takes place in two stages. In the first stage, which is more effective below 500°C, the

Contd...

organic sulfur decomposes to hydrogen sulfide by the action of heat only and desulfurization is of the order of 25 - 30%. In the second stage, the gases which are evolved during carbonization influence further desulfurization amounting upto 50%.

4. Also, a portion of the organic sulfur compounds decomposes to volatile sulfur compounds. Most of these compounds appear in the tar produced during carbonization.

He used the same apparatus to study the effect of hydrogen on desulfurization of coal during carbonization. He studied four coal samples of different sulfur contents varying from 0.75 to 1.82%. It was shown that during coking operation passage of hydrogen gas gave better desulfurization. During these studies using hydrogen, Powell made the following observations:

1. Iron pyrite is caused to decompose at a lower temperature. The decomposition being practically complete at 500°C.
2. The decomposition of organic sulfur is very little affected below 500°C, but is enormously increased from 500 - 1000°C.

Snow (4) investigated the desulfurization action of fourteen different gases and vapors on coal using a fixed-bed. He showed that ammonia, hydrogen, steam and water-gas, all of which give hydrogen either in molecular or in nascent form give better desulfurization. While studying with hydrogen Snow observed that even at 400°C the effect of hydrogen on desulfurization of coal was quite evident. At about 500°C the desulfurization attained an apparent maximum of 65-70%. Further noticeable desulfurization started

after about 1000°C. At 1000°C, desulfurization action of hydrogen was found to be 87%. In the case of ammonia, it was found that temperatures about 600°C were favourable for desulfurization. At 1000°C about 82% desulfurization was obtained. Water gas was also quite effective particularly at temperatures above 800°C. However, the losses of coal because of gassification were high.

Ghosh and Brewer (5,6) took Assam and Illinois coals for their studies. The significant difference between these two coals was that while Assam coal contained about 90% organic sulfur and 10% inorganic sulfur, the Illinois coal contained approximately equal proportions of sulfur in organic and inorganic form.

Their apparatus consisted of a 24 mm diameter silica reactor tube placed inside an electrically heated furnace. The reactor tube was provided with a perforated porcelain tube on which coal rested. With Illinois coal they observed that ammonia gave better desulfurization and the rate increased with temperature up about 800°C steadily, after which there was no appreciable change in the desulfurization. They found that the desulfurization action decreased from gas to gas in the order of ammonia, hydrogen and nitrogen. They also observed that above 800°C the desulfurization action of these gases was less. They attributed this behaviour to the reaction of hydrogen sulfide with coke to form stable sulfur compounds at temperatures above 800°C. They arrived at the same conclusions with Assam coal. They also noticed that when coal was mixed with lime or sodium carbonate the percentage of sulfur removal from Assam coal was greater than that of the coal without these added compounds. However Illinois coal showed the opposite effect.

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Ghosh and Brewer further pointed that the composition of ash in the coal determines to some extent the extent of desulfurization. While coals with iron oxide as the major constituent in their ash were lesser desulfurized, coals whose ash was of higher alumina content showed higher desulfurization. A possible explanation given by them is that sulfur forms stable compounds with iron oxide while unstable compounds are formed with alumina.

Goswami and Roy (7,8) made desulfurization studies on Assam coal using fixed-bed carbonizer. They used coal from Baragoli colliery which contained 4.57% total sulfur of which 87% was in the organic form. The particle size of the coal they used was -60+80 mesh. They mixed coal with silica and sodium silicate, respectively as catalysts in various proportions and then carbonized the resulting mass. They observed that in both cases the desulfurization increased with an increase in the catalyst concentration upto a certain level after which a further increase caused low desulfurization.

Their work also included passing of coal gas through the fixed coal bed with and without the addition of various catalysts. The catalysts they used were sand, sodium silicate, calcium oxide, mixtures of magnesium chloride and calcium oxide and hydrated alumina. It was observed that in the presence of coal gas, desulfurization of coal increased by about 30% when carbonization was carried at about 800°C for 6 hours. Under the same conditions of carbonization when coal was mixed with 5% sand, the increase in desulfurization was about 15%. They found that the amount of catalyst in coal bed did not affect desulfurization appreciably. In presence of hydrated alumina at a concentration of 0.5% by weight the desulfurization was about 80% when coal was carbonized in presence of coal gas at 850°C. Under the same conditions coal with 5% sand gave 67% desulfurization.

Coal desulfurization in a fluidized bed was studied by Jacob and Minker (9). They performed experiments on a bench scale with high sulfur bituminous coal. The fluidized bed reactor was a vertical stainless steel tube of 1½" in diameter which was placed in an electrically heated muffle furnace. The fluidizing medium was a mixture of air, nitrogen, and steam in various proportions. Their results can be summarized as follows:

1. Smaller the particle size of the charge, the better was the desulfurization.
2. Desulfurization increased with increased fluidization velocity upto certain point after which the increase in velocity had no effect.
3. Steam in the fluidizing medium did not have much influence on the desulfurization.
4. At air concentration below 5% in the fluidizing medium the coal agglomerated. Desulfurization increased with increased air concentrations from 5 to 20%. But above 20%, the sulfur removal was not appreciable. Above 60% air concentrations, the combustion of coal was excessive.

E X P E R I M E N T A L

Apparatus

A schematic diagram of the apparatus set up is given in Fig. 1. Figs. 2 and 3 show the photographs of the apparatus. The apparatus mainly consisted of a fluidized bed reactor, a preheater, and an assembly of flow meters.

The fluidized bed reactor consisted of two parts. The lower part of the reactor, as shown in Fig. 4, was of 3.4 cm in diameter and 52 cm in length. About 3 cm from the bottom of the tube the wall of the vycor tube was made to project inside at a number of locations so that they formed a support to place a stainless steel screen. This screen held a 2 cm bed of steel balls of 0.32 cm in diameter. The steel bed acted as a porous medium for proper and uniform distribution of gases that enter the bottom of the reactor to effect good fluidization of coal. To the upper end of the vycor tube, a 50/50 pyrex standard joint was connected properly through a gradation seal. A 8 mm diameter tube passed through the female part of the joint and carried a thermocouple wire.

The reactor was properly placed in an electrically heated laboratory made vertical tubular furnace, which was regulated by a "Honeywell" controller. A horizontal electrically heated furnace with a 1 $\frac{1}{2}$ " diameter steel pipe contained in it acted as a preheater for the fluidizing gases before they entered the reactor.

A manifold consisting of four rotameters measured the flow rates of different gases. However only three of these rotameters were used in the present study.

1. Diaphragm valve
2. Press. gauge
3. Flow regulating valve.
- 4-7. Rotameters
8. Preheaters.
9. Horizontal tube furnace.
10. Reactor
11. Vertical tube furnace.
12. Outlet gas cooler.

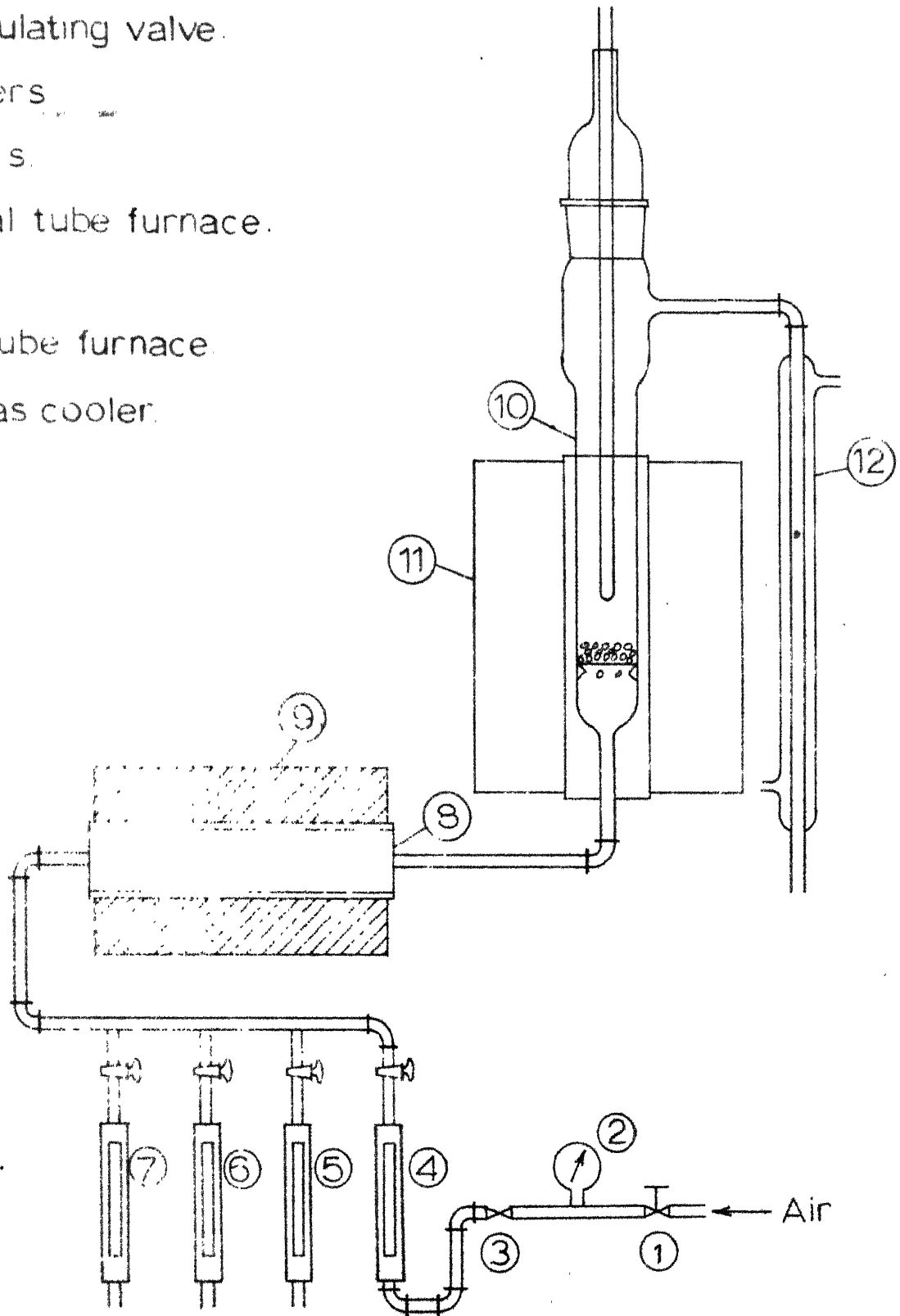


Fig.1 - Schematic diagram of the fluidized-bed apparatus.

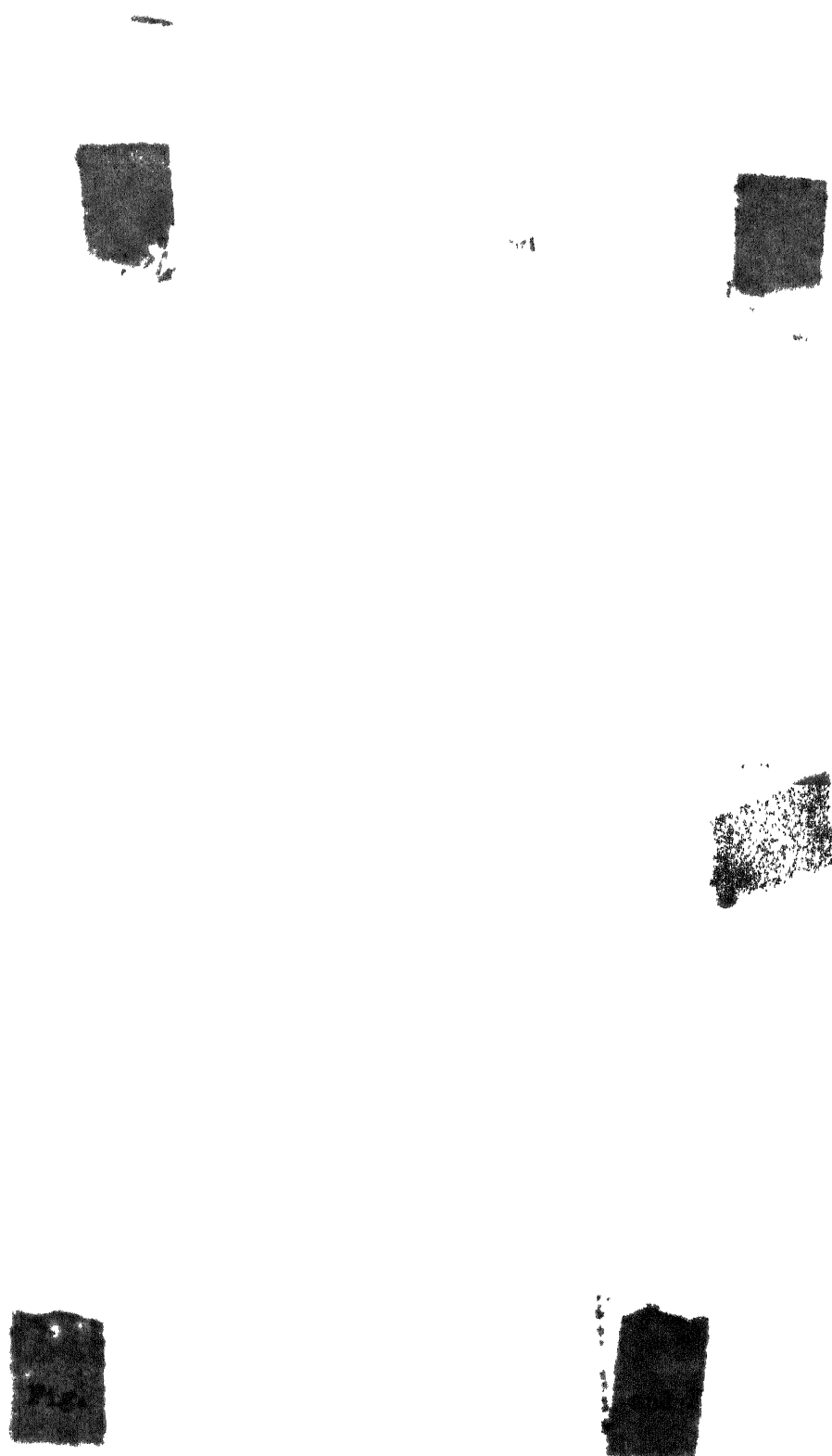


Fig. 2 Photograph showing the Flowmeters and Controllers

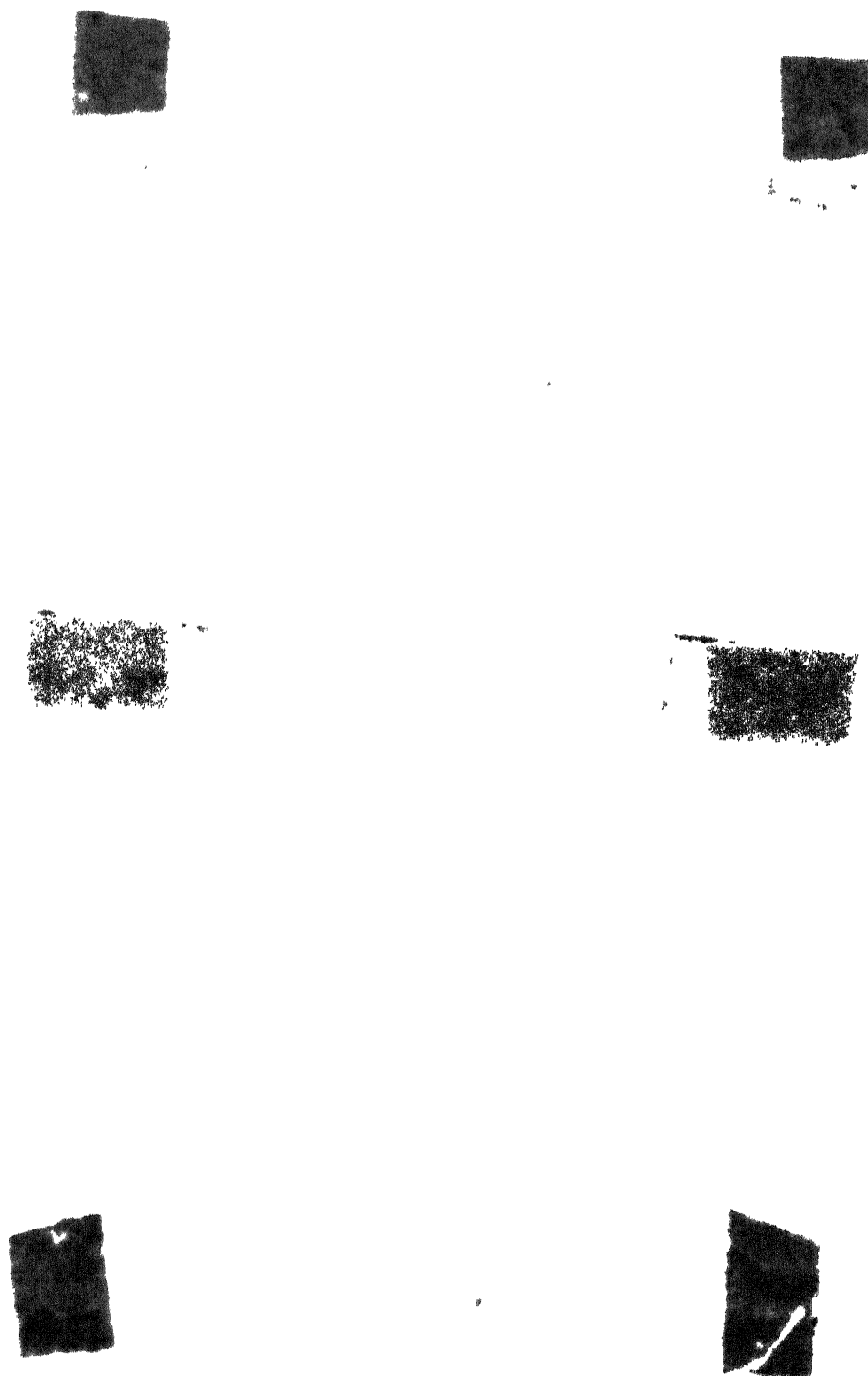


Fig. 3 Photograph showing the Preheater and Fluidized Bed Reactor

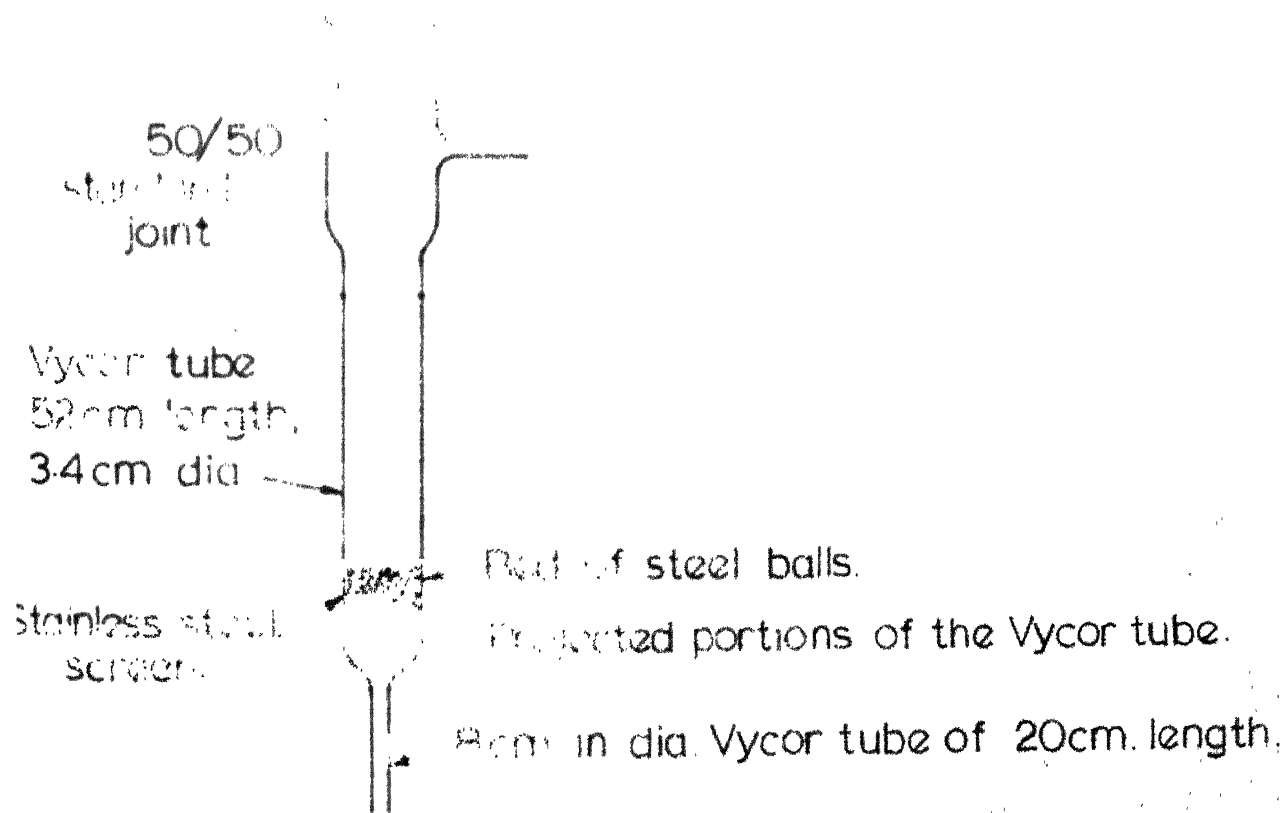
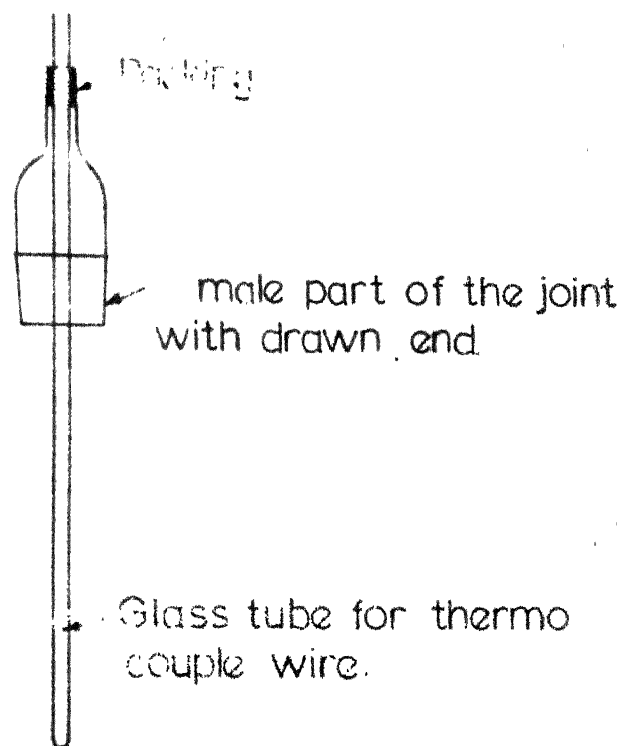


Fig.4.- Detailed sketch of the fluidized-bed reactor.

Procedure

Initially air in proper amount as measured by one of the rotameters was passed into the reactor through the preheater. The outlet temperature of the gas from the preheater was about 500°F. The flow rate of air in liters/min. was maintained at a value equal to the flow rate of the gases that were used for fluidization. After the desired temperature was reached in the reactor, the air flow rate was cut off and simultaneously nitrogen was admitted at a smaller rate so that an inert atmosphere was maintained in the reactor. Under these conditions a charge of 10 gms. coal of -25+36 mesh size was fed into the reactor very quickly and the desired fluidizing gas at the required flow rate was turned on cutting off the nitrogen supply. Thus a run was made to progress. During the charging period the temperature of the reactor fell below the desired value by about 100°C. However after about one to two minutes the reactor reached its desired condition.

All the runs were generally carried out for a duration of fifteen minutes. During the course of the run, the temperature of the reactor was checked periodically so that it maintained correctly. The temperature was maintained within $\pm 5^{\circ}\text{C}$ of the desired value. At the end of the run, the supply of the fluidizing gas was cut off and the coal was withdrawn from the reactor by applying suction. During this process, a very small amount of nitrogen was admitted into the reactor again for the purpose of maintaining inert atmosphere.

The resulting coal after withdrawal from the reactor was analysed for its sulfur content. The sulfur analysis was done by the

standard Eschka method with a few minor modifications as outlined in the references 10 and 11.

Experimental Programme:

The coal that was used in this investigation was supplied by Coal Survey Station, Jorhat, Assam. The properties of the coal were as given below:

Moisture	2.37%
Volatile matter	37.2 %
Ash	6.3 %
Fixed carbon (by difference)	54.13%
Total sulfur	4.75%
Composition of sulfur	
Sulfate sulfur	2.77%
Pyritic sulfur	9.13%
Organic sulfur (by difference)	88.20%

During the preliminary investigations it was found that the coal particles agglomerated at about 500°C into a coherent mass in the reactor even in the presence of fluidizing gases. Therefore it was felt necessary to avoid this situation and see that the coal is fluidized properly. Studies indicated that initial oxidation of the coal reduced the caking property sufficiently. The resulting oxidized coal, devoid of some of its volatile content, was found to fluidize easily. After several attempts, it was found that the coal resulting from oxidation at 450°C for about 10 minutes was suitable for the present study. The sulfur content in the oxidized coal thus obtained was determined to be 4.25% by weight compared to 4.75% in the original coal.

The fluidizing gases that were used in this study were mainly nitrogen and ammonia. In order to study the effect of dilution of ammonia with nitrogen on desulfurization rates, few experiments were conducted using mixtures of ammonia and nitrogen in various proportions. For each of these media, a flow rate of 31.2 cm./sec. calculated at STP was found to be suitable for good fluidization. Several runs were made using these gases at various temperatures ranging from 400-700°C. At some of the experimental conditions, duplicate runs were made to ensure reproducibility of the results.

RESULTS AND DISCUSSION

The experimental data that were obtained in this study are given in Tables 1, 2 and 3. Also included in these tables are calculated values of the percentage desulfurization and percentage sulfur retention which are defined as:

$$\% \text{ desulfurization} = \frac{\% \text{ S in the initial coal} - \% \text{ S in the resulting char}}{\% \text{ S in the initial coal}} \times 100$$

$$\text{and } \% \text{ sulfur retention} = 100 - \% \text{ desulfurization}$$

$$\text{or} = \frac{\% \text{ S in the char}}{\% \text{ S in the initial coal}} \times 100$$

In general, the reproducibility of the results was good as is evident from Runs 3 & 3a, 4 & 4a, 6 & 6a, 8 & 8a, and 14, 14a & 14b.

The experimental results show that the % desulfurization increases with temperature immaterial of the fluidizing medium. However, the % desulfurization in the case of nitrogen is very poor even at the maximum temperature of 700°C that was tried in this study. Nitrogen, being inert does not take part in any chemical reaction with sulfur compounds in the coal to enhance the sulfur removal rates. It only acts as a fluidizing medium. However, some desulfurization will take place because of the decomposition of sulfur compounds present in the coals.

TABLE : 1

EXPERIMENTAL RESULTS USING NITROGEN AS THE FLUIDIZING MEDIUM

Experimental conditions:

Initial charge of the coal to the reactor = 10 gms.

Sulfur content of the charge = 4.25%

Fluidizing velocity = 31.2 cm/sec.

Time of operation = 15 minutes.

Run No.	Temperature °C	Sulfur % in char	% desulfurization	% sulfur retention
1	455	4.11	3.4	96.6
2	500	3.94	7.4	92.6
3	600	3.86	9.1	90.9
3a	600	3.81	10.4	89.6
4	700	3.67	13.6	86.4
4a	700	3.71	12.7	87.3

TABLE : 2

EXPERIMENTAL RESULTS USING AMMONIA AS THE FLUIDIZING MEDIUM

Experimental conditions:

Initial charge of the coal to the reactor = 10 gms.
 Sulfur content of the charge = 4.25%
 Fluidizing velocity = 31.2 cm./sec.

Run No.	Temperature °C	Time in minutes	Sulfur % in char	% desulfurization	% sulfur retention
5	400	15	3.98	6.4	93.6
6	500	15	3.81	10.4	89.6
6a	500	15	3.88	8.7	91.3
7	600	15	3.51	17.4	82.6
8	700	15	2.26	46.8	53.2
8a	700	15	2.23	47.5	52.5
9	700	40	2.28	46.4	53.6

TABLE : 3

EXPERIMENTAL RESULTS USING AMMONIA - NITROGEN MIXTURES AS THE FLUIDIZING MEDIA

Experimental conditions:

Initial charge of the coal to the reactor = 10 gms.

Sulfur content of the charge = 4.25%

Run No.	Ratio of $\text{NH}_3:\text{N}_2$ by volume.	Fluidizing velocity cm./sec.at STP	Temperature °C	Time in minutes.	Sulfur % in char.	% Desulfurization.	% Sulfur retention
10	1:1	31.2	600	15	3.52	17.2	82.8
11	1:3	31.2	600	15	3.53	17.0	83.0
12	1:3	31.2	600	25	3.52	17.2	82.5
13	1:3	31.2	700	15	2.29	46.1	53.9
14	1:4.45	45.0	600	15	3.32	21.9	78.1
14a	1:4.45	45.0	600	15	3.57	16.0	84.0
14b	1:4.45	45.0	600	15	3.55	16.5	83.5
15	1:4.45	45.0	600	25	3.50	17.5	82.5

As is to be expected, ammonia because of its hydrogen content gave better desulfurization action than nitrogen. However, at lower temperatures the removal of sulfur is very poor. The % desulfurization varies slowly from approximately 6 to 18% in the temperature range of 400 to 600°C. When the temperature is raised from 600 to 700°C it is seen that there is a sudden rise in the % desulfurization from 17.4 to 47.5%. This is in accordance with the observations made by the previous investigators (e.g. 4) that, the desulfurization action of ammonia is better at temperature above 600°C.

The experimental results using nitrogen, and ammonia are presented in Figs. 5 and 6 respectively. These plots are intended not for any correlation purposes, but to show the trend of the desulfurization behaviours in the two cases.

The effect of nitrogen dilution in ammonia is found to be negligible in the desulfurization process. This is evident from the data of two sets of runs namely, 7, 10, & 11, and 8 & 13 respectively. While the former set of runs were made at a temperature of 600°C the latter were made at 700°C. In both the cases, the velocity of the fluidizing media and the time of operation were kept same at 31.2 cm./sec. and 15 minutes. Desulfurization remained constant at 600°C at a value of 17% even though the ammonia-nitrogen ratio was varied from 1:0 to 1:3. Similarly at 700°C, the value was constant at about 46% when the same ratio was changed from 1:0 to 1:3.

Also it is seen that the fluidizing velocity has no effect on the desulfurization. This is evident from the results of the run 14 and the set of runs 7, 10 & 11. In run 14, the fluidizing velocity of the

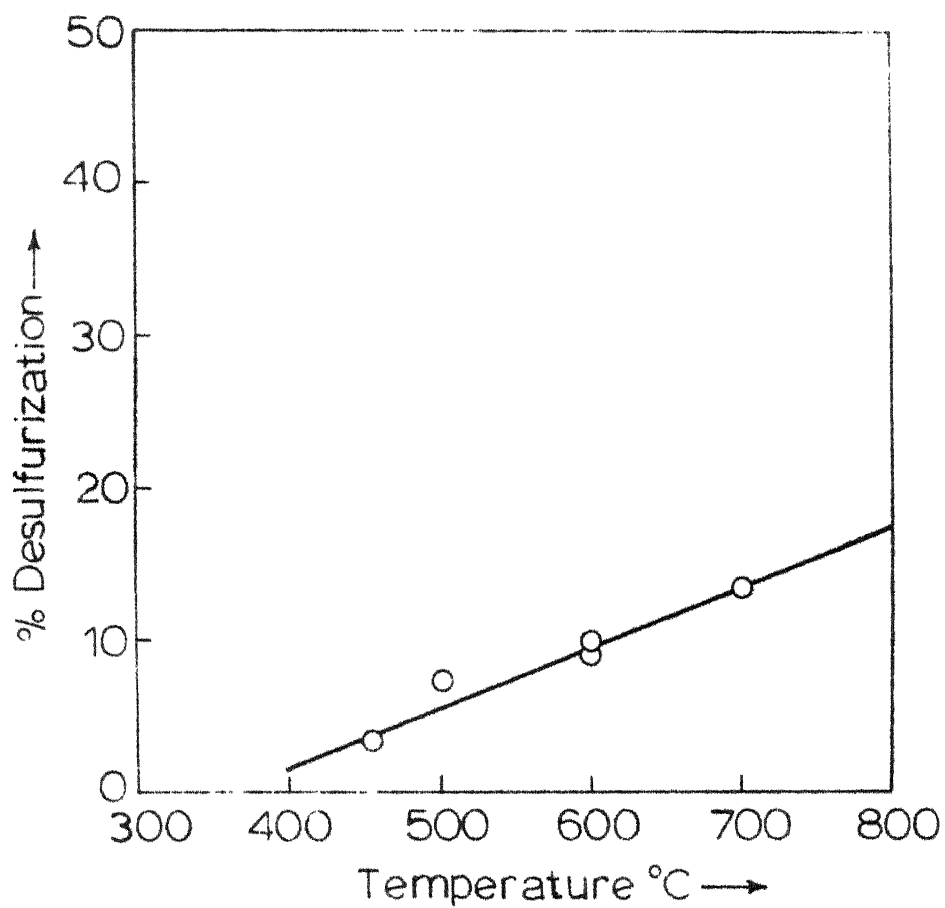


Fig.5 -% Desulfurization vs. Temperature plot using N₂ as fluidizing medium.

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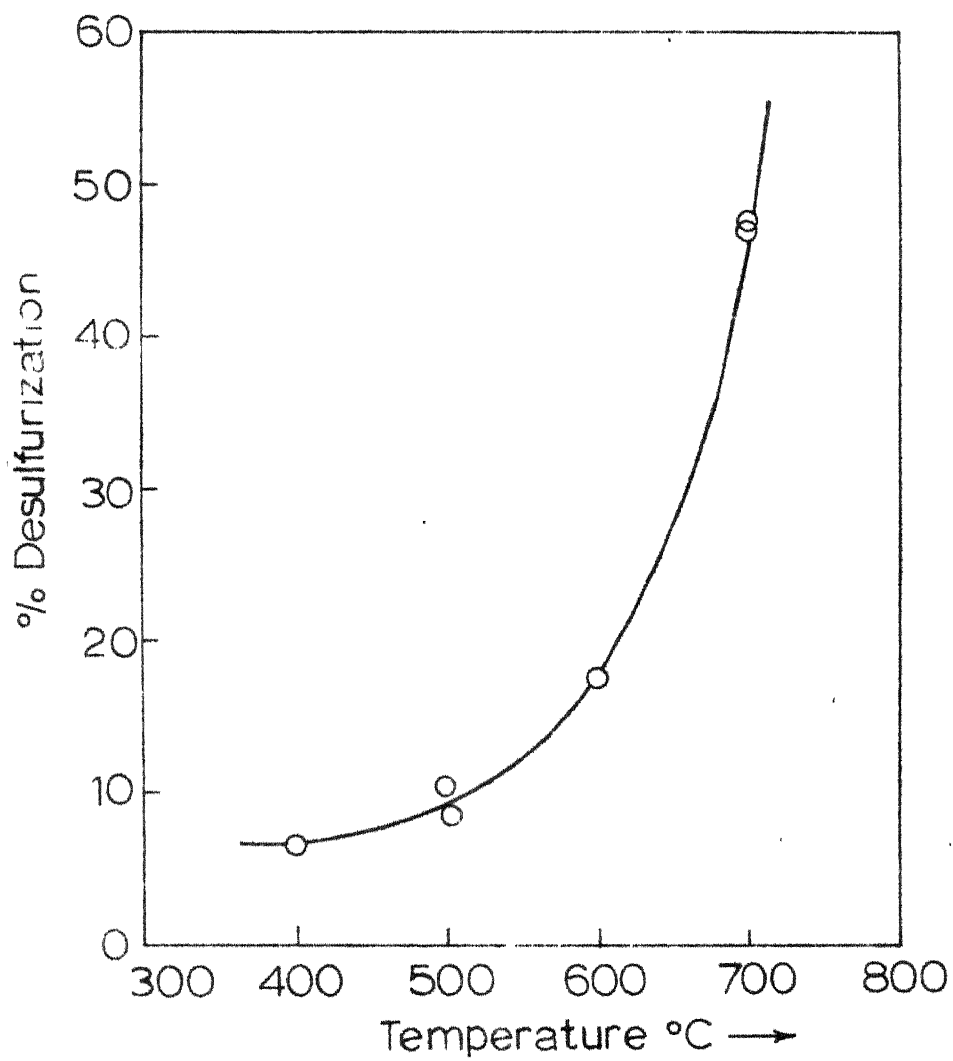


Fig. 6 - % Desulfurization vs. Temperature using NH_3 as fluidizing medium.

1:4.45 ammonia - nitrogen mixture was maintained at 45.0 cm./sec.

Otherwise, the experimental conditions were same for these runs. This observation together with the one made above, indicate that the desulfurization action of ammonia would not vary with nitrogen dilution in the range of zero to about 80% by volume.

The data of the runs 8 & 9, and 11 & 12 show slight discrepancies in the experimental results. The results indicate that desulfurization is more at lower times of operation than at longer times. However, the discrepancies are very small and probably can be attributed to the experimental errors. If these are discounted, the results show that the operation time of carbonization has no effect on the final composition of the resulting char.

The results from this investigation can then be summarized as:

1. Desulfurization increases with temperature.
2. Ammonia is a better desulfurization medium than nitrogen.

However, the amount of desulfurization is same whether pure ammonia or ammonia - nitrogen mixture with 80 volume percent nitrogen is used as the fluidizing medium.

3. The fluidization velocity has no effect on desulfurization.
4. Within experimental accuracy, the operation time also has no effect on desulfurization.

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APPENDIX

(i) Determination of sulfur percentage in coal sample.

Sulfur was determined by Eschka method which is as follows:

In a porcelain crucible exactly 1 gm. of the sample was mixed with 3 gms. of Eschka mixture which was prepared by mixing 2 parts by weight of CaO (instead of MgO as used commonly) with 1 part by weight of anhydrous Na_2CO_3 . The mixture of the crucible was covered with 1 gm. of the Eschka mixture. The contents were heated gradually to 800°C and then kept at that temperature for one hour. The crucible was then cooled and the contents were transferred to a beaker and boiled for five to ten minutes with distilled water rather than with bromine water as is outlined in the original Eschka method. This modified method is suggested by other workers(11). The solid materials were then dissolved in HCl and the solution was neutralized with strong NH_4OH solution with methyl orange as indicator, and then 4 ml. of HCl was added. The solution was boiled gently and in the boiling condition 10 ml. of 10% Ba Cl_2 solution was added. Boiling was continued for some time so that the resulting Ba So_4 precipitate became granular. The precipitate was filtered and the weight of the Ba So_4 was determined.

A blank run was carried out similarly and the percentage of sulfur was determined as:

$$\% \text{ of sulfur} = 13.74 (W_1 - W_2)$$

where W_1 = weight of Ba So_4 in actual run, gm.

W_2 = weight of Ba So_4 in blank run, gm.

(ii) Determination of the forms of sulfur in coal sample.

Sulfate Sulfur:

5 gm. of the coal sample was boiled with 50 ml. of 5N HCl for 30 minutes. The contents were filtered and to filtrate 2 ml. of 100 volume

H_2O_2 was added and boiled for 5 minutes. The solution was neutralized with 5 N NH_4OH using methyl red as indicator. After the end point, 5 drops of excess NH_4OH were added to the solution. The precipitate was filtered. The filtrate was neutralized with HCl and then 1 ml. of HCl in excess was added to the neutralized solution. The solution was boiled and was mixed with 10 ml. of 10% BaCl_2 solution. The resulting BaSO_4 precipitate was filtered and its weight was determined.

Similarly a blank run was carried out and the percentage of the sulfate sulfur was determined as follows:

$$\% \text{ of sulfate sulfur} = \frac{W_2 - W_3}{W_1} \times 13.74$$

where W_1 = weight of the coal sample, gm.

W_2 = weight of the BaSO_4 from actual run, gm.

W_3 = weight of the BaSO_4 from blank run, gm.

Pyritic and Organic Sulfur:

The residue from sulfate sulfur determination was boiled with 200 ml. of 2N HNO_3 for about 30 minutes. After filtration, the filtrate was boiled for 5 minutes with 5 ml. of 100 volume H_2O_2 . The solution was neutralized with strong NH_4OH using methyl red as indicator and 5 drops of NH_4OH were added in excess. The filtered precipitate was dissolved in small quantity of 5N HCl. The solution was diluted to 250 ml. and 50 ml. portion was taken for pyritic sulfur determination.

The 50 ml. solution was heated to boiling and 5% stannous chloride in 5N HCl was added drop by drop untill the yellow colour disappeared. 5 drops of stannous chloride solution were added in excess and the solution was cooled. The solution was mixed rapidly with saturated mercuric chloride solution. The resulting mixture was treated with N/50 potassium dichromate solution, using sodium-diphenyl amine sulfonate in sulfuric/phosphoric acid as internal indicator. Percentage of the pyritic sulfur was calculated

as follows:

$$\% \text{ Pyritic sulfur} = \left(\frac{5 \times V}{W_1} \right) \times 0.1311 W$$

where W = wt. of $K_2 Cr_2 O_7$ / litre, gm.

W_1 = wt. of coal used, gm.

V = volume of $K_2 Cr_2 O_7$ used to titrate 50 ml. of the solution, ml.

Organic sulfur was determined by difference as:

$$\% \text{ of organic sulfur} = \% \text{ total sulfur} - (\% \text{ sulfate sulfur} + \% \text{ Pyritic sulfur})$$